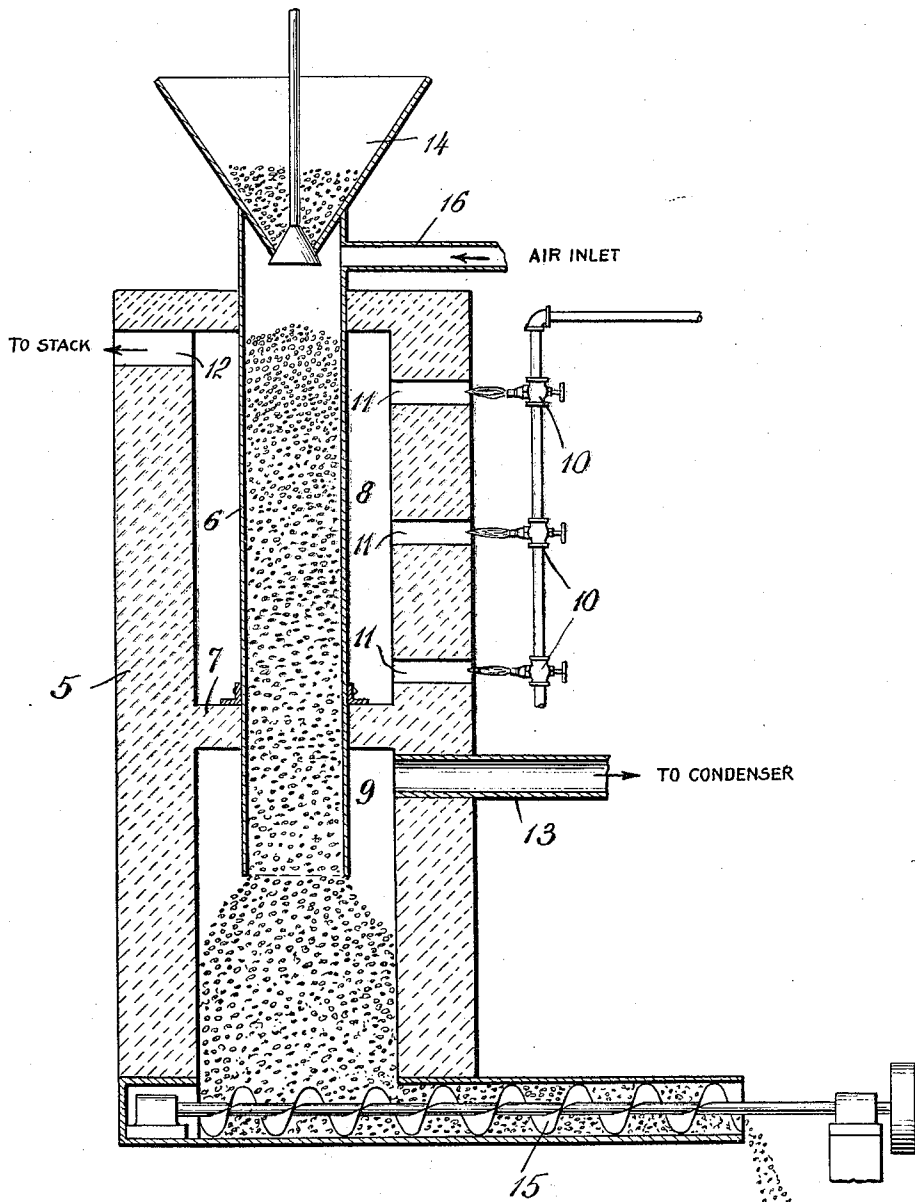


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METHOD OF EXTRACTING AND RECOVERING MOLYBDENUM FROM ITS ORES AND CONCENTRATES.
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1,299,560.

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UNITED STATES PATENT OFFICE.

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METHOD OF EXTRACTING AND RECOVERING MOLYBDENUM FROM ITS ORES AND CONCENTRATES.

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Specification of Letters Patent.

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To all whom it may concern:

Be it known that I, HENRY ALFRED DOERNER, a citizen of the United States, residing at Denver, in the county of Denver and State of Colorado, have invented certain new and useful Improvements in Methods of Extracting and Recovering Molybdenum from Its Ores and Concentrates; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

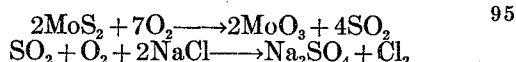
The present invention relates to the extraction and recovery of molybdenum from its ores and concentrates, and in particular to the extraction and recovery of molybdenum in the form of molybdenum oxid of commercial purity from ores of molybdenum containing sulfur, such, for example, as molybdenite, the molybdenum sulfid ore. The invention has for its object the provision of an improved method for the extraction and recovery of molybdenum from its ores and concentrates, and more particularly the provision of an improved method for the extraction and recovery of molybdenum from ores or concentrates containing sulfur in combination with the molybdenum or in some other form.

It has heretofore been proposed to recover molybdenum from its oxid ores by heating a mixture of the ore with a suitable chlorid and distilling off the molybdenum in the form of volatile chlorids. I have found that the recovery of molybdenum by this general process is very materially increased if suitable agents are employed for facilitating the liberation of chlorin from the chlorid mixed with the ore. For example, I have found that this liberation of chlorin may be electrolytically effected by passing an electric current through a molten bath of the mixed ore and chlorid, as described in my copending application for Letters Patent of the United States filed January 18, 1917, Serial Number 143,081. The present application is a continuation in part of this copending application and relates particularly to the use of sulfur either combined in the ore itself or added thereto in some form or other for effecting the liberation of chlorin from the chlorid mixed with the ore.

I have discovered that when molybdenum ores or concentrates or other appropriate

molybdenum-containing materials are given an oxidizing roast with a suitable chlorid in the presence of sulfur, either naturally combined in the ore or added thereto in some form free or combined, the molybdenum will distil off in the form of volatile chlorids or oxy-chlorids, and the distillation of the molybdenum will be practically complete. If the molybdenum ore is poor in sulfur and no additional sulfur-containing material is added to the charge, the yield of molybdenum chlorid distillate is only slight, and accordingly in the case of such ores I add a suitable amount of sulfur in some form or other for effecting a sufficient liberation of chlorin to react with substantially all of the molybdenum content of the ore.

In the practice of the invention with a sulfid ore of molybdenum, such, for example, as molybdenite, the ore, mixed with additional sulfur-containing material if necessary, is given an oxidizing roast in the presence of a suitable chlorid, such, for example, as commercial sodium chlorid or common salt. The presence of the sulfur in the charge together with the oxidizing atmosphere which is maintained during the treatment results in the liberation of free chlorin in two stages or reactions. In the first stage, or reaction, the sulfur in the charge is converted by the oxidizing roast into sulfur dioxid, and in the second stage or reaction, this sulfur dioxid together with additional oxygen reacts with the chlorid to liberate chlorin. These two stages or reactions may be represented by the following equations, in which it is assumed that all of the sulfur needed for the operation is contained in the ore:



The chlorin thus formed as a result of the oxidizing roast in the presence of a sulfur-containing material is set free within the mass of the ore where it can easily combine with the molybdenum to form volatile compounds.

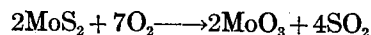
The process of my present invention can with advantage be combined with that of my aforementioned copending application in which chlorin is electrolytically liberated. Thus the presence of sulfur-containing materials, either in the ore itself or added thereto, in the fused bath of ore and chlorid

mixture will supplement the electrolytically formed chlorin, thereby effecting an economy in the amount of chlorin which must be electrolytically produced. In practising the invention of my copending application with ores containing sulfids, such as molybdenite, I, therefore, admit air to oxidize the sulfur and form chlorin, as hereinabove explained, and thereby supplement the supply of electrolytic chlorin. Thus, where, under non-oxidizing conditions the sulfur of the molybdenum sulfid may combine with the chlorin to form sulfur chlorid, under such oxidizing conditions as are maintained in the practice of my present invention, it may be oxidized to sulfur dioxide so that less electrolytically produced chlorin is required for the reaction. For example, where the mixture of molybdenite and salt is heated to fusion, and subjected to an oxidizing atmosphere by injecting air into the fused bath, the sulfur dioxide formed by the oxidizing atmosphere and the sulfur of the sulfid (molybdenite) reacts with more oxygen and with the salt to form chlorin, which latter combines with the molybdenum to form volatile compounds that distil off. Thus the reaction of the sulfur, oxygen (from the oxidizing atmosphere) and salt furnishes or sets free chlorin which augments the chlorin set free by electrolysis.

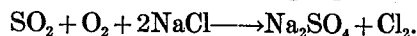
In the figure of the accompanying drawings, I have illustrated the improved apparatus which I have devised for practising the method of the present invention. This apparatus comprises an outer wall 5 of brick or other suitable material, and an inner ore chamber or tube 6 which may be formed of iron. The outer wall 5 and inner tube 6 may be of cylindrical or any other desired or convenient cross-section. The inner tube 6 is of smaller diameter or width than the interior of the outer wall part 5, and the space between these two members is divided into two compartments by means of a shelf 7 located about midway between the top and bottom of the wall 5 and preferably integral therewith. The parts thus described form a vertical kiln furnace in which the upper compartment 8 of the space between the wall 5 and tube 6 is utilized as a combustion chamber, and the lower compartment 9 is employed as a volatilizing chamber. To this end suitable burners 10 are provided in proximity to ports 11 in the wall 5, and an outlet 12 to a stack or the like is provided for the exhaust products of combustion from the chamber 8. A suitable conduit 13 communicates with the volatilizing chamber 9 for carrying away the volatilized compounds. A hopper 14 for feeding the charge into the tube 6 is operatively arranged at the top thereof, and a screw 15 is provided at the bottom of the furnace for carrying away the treated ore. An air inlet 16 is

provided near the top of the tube 6 through which a supply of air may be admitted to the tube for effecting the reactions of my present invention.

In the preferred practice of the invention, the finely ground molybdenum ore is mixed with a suitable chlorid, such, for example, as common salt, and if poor in sulfur content, sulfur is added thereto in some form free or combined. The mixture is made into a thick mud with water and briqueted. The dry briquets are placed in the hopper 14 and fed into the vertical kiln furnace illustrated in the accompanying drawings. The ore passes down through the furnace by gravity at a rate governed by the screw discharge. A down draft current of air, obtained either by suction or pressure, produces oxidation and carries the distillate to a suitable condenser. An important feature of the vertical kiln furnace illustrated in the accompanying drawings is the provision for the travel of the air and ore in the same direction, since this allows the sulfur dioxide, which is liberated in the upper part of the furnace, a maximum opportunity to react with the salt in the lower and hotter part of the furnace. Thus in the upper part of the furnace, the first stage or reaction of my improved method takes place which is represented by the following equation:



and a little lower the second stage or reaction of the method takes place which is represented by the following equation:



The chlorin thus liberated reacts with the molybdic oxid at once or passes down and volatilizes any molybdenum which may still remain in the lower part of the furnace. A further advantage of the down draft is that the distillate leaves the ore at a point where the latter is in a semi-fused condition, thus giving no chance for dust to contaminate the distillate.

The briqueting of the ore permits an intimate mixture of the reacting substances and at the same time allows a free passage of air through the furnace without dust. In order that the reactions may penetrate to the center of the briquets, I prefer to make the briquets less than one inch in thickness and to regulate the operation of the furnace so that the briquets remain in the heated zone for two hours or more.

The molybdenum chlorids or oxy-chlorids which pass off to the condensing chamber are decomposed therein into molybdenum oxid and hydrochloric acid by the action of steam or water. This decomposition of the molybdenum chlorids and the formation of the oxids and hydrochloric acid may with advantage be carried on in the condensing

chamber itself. The hydrochloric acid can be separated by evaporation or distillation and recovered, leaving behind the molybdenum oxid. Inasmuch as molybdenum also forms a number of oxids, as well as a number of volatile chlorids, the final product will vary according to the variations in the chlorid distillate.

While I have described a type of furnace particularly adapted to the practice of the invention, I do not desire to limit myself to the use of any particular type of furnace, since it will be evident that the method of the invention may be carried out in other types of furnaces. I wish it also to be understood that while I have described my invention more particularly with the use of sodium chlorid, other suitable chlorids, fusible or infusible, are adapted for use in the process.

The charge consisting of the molybdenum-containing material together with a source of sulfur, that is, together with sulfur either naturally combined with the molybdenum-containing material or added thereto, admixed with the chlorid should be fed into the furnace in a lumpy or agglomerated condition in order that free passages may be provided between such lumps of the mixed charge for the air draft. The briquetting of the charge is therefore of importance for the satisfactory operation of the process, and particularly when the process is carried out in the type of furnace illustrated in the drawing.

What I claim is:

1. The method of treating molybdenum ores, concentrates and other molybdenum-containing materials, which comprises heating the material under oxidizing conditions in the presence of a chlorid and a source of sulfur so that the sulfur reacts to effect the liberation of free chlorin which combines with the molybdenum to form volatile chlorids or oxy chlorids; substantially as described.

2. The method of treating molybdenum sulfid ores, concentrates and other molybdenum-sulfid-containing materials, which comprises heating such materials in the presence of a chlorid and under oxidizing conditions to a sufficient temperature to set free chlorin and to volatilize the molybdenum in the form of chlorids or oxy chlorids; substantially as described.

3. The method of treating molybdenum sulfid ores, concentrates and other molybdenum-sulfid containing materials, which comprises heating the material with a chlorid under oxidizing conditions to a sufficient temperature to set free chlorin and volatilize the molybdenum as chlorid or oxy chlorid and forming molybdenum oxid therefrom by the action of steam or water; substantially as described.

4. The method of treating molybdenum ores, concentrates and other molybdenum-containing materials, which comprises heating such materials in combination with a suitable source of sulfur and mixed with a source of chlorin under oxidizing conditions and thereby liberating chlorin through the interaction of oxygen and sulfur with said source of chlorin and forming volatile chlorids of molybdenum; substantially as described.

5. The method of treating molybdenum ores, concentrates and other molybdenum-containing materials, which comprises feeding such material in combination with a source of sulfur and mixed with a chlorid into the top of a vertical chamber, supplying heat to the upper part of said chamber while maintaining a down draft of air there-through and thereby liberating chlorin through the interaction of oxygen and sulfur with said chlorid and forming volatile chlorids of molybdenum, and drawing off from the bottom of said chamber the volatile chlorids of molybdenum so formed; substantially as described.

6. The method of treating molybdenum ores, concentrates and other molybdenum-containing materials, which comprises heating a charge of the material with a source of sulfur and a source of chlorin, maintaining a draft of air through the charge during the heating whereby chlorin is liberated within the charge by the interaction of oxygen and sulfur with the source of chlorin, and maintaining the heating of the charge to a sufficient temperature for the free chlorin thus liberated within the charge to form volatile chlorids of molybdenum; substantially as described.

7. The method of treating molybdenum-sulfid ores, concentrates and other molybdenum-sulfid-containing materials, which comprises mixing the material in a finely divided state with a chlorid and briquetting the mixture, and heating the briquetted mixture under oxidizing conditions and thereby liberating chlorin from said chlorid through the interaction therewith of the sulfur of the ore and oxygen and thereby forming volatile chlorids of molybdenum; substantially as described.

8. The method of treating molybdenum-containing materials, which comprises briquetting the molybdenum-containing material together with a source of sulfur and admixed with a chlorid, and heating the briquets under oxidizing conditions to a sufficient temperature to set free chlorin and to volatilize the molybdenum in the form of chlorid or oxy chlorids; substantially as described.

9. The method of treating molybdenum-containing materials, which comprises briquetting the molybdenum-containing mate-

rial together with a source of sulfur and admixed with sodium chlorid, heating the briquets and maintaining during such heating a draft of air through the briquets whereby the interaction of oxygen with the sulfur and the sodium chlorid of the charge liberates chlorine within the charge and forms volatile chlorides of molybdenum; substantially as described.

10 10. The method of treating molybdenum-containing materials, which comprises briquetting the molybdenum-containing material together with a source of sulfur and admixed with sodium chlorid, feeding the briquets into the top of a heated chamber through which a downward draft of air is maintained whereby volatile chlorides of molybdenum are formed and conducted away from the bottom of said chamber, and

withdrawing the spent charge from the bottom of said chamber; substantially as described. 20

11. The method of treating molybdenum-containing materials, which comprises feeding such material together with a source of sulfur and admixed with a chlorid into the top of a heated chamber, maintaining a downward draft of air through the charge in said chamber, thereby liberating chlorine from said chlorid through the interaction therewith of the sulfur of the charge and oxygen and forming volatile chlorid of molybdenum, withdrawing the volatile chlorides of molybdenum from the bottom of said chamber, and withdrawing the spent charge from the bottom of said chamber; substantially as described. 25 30 35

HENRY ALFRED DOERNER.